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Published in:
Applied Physics Letters

DOI:
10.1063/1.117478

Publication date:
1996

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Citation: Appl. Phys. Lett. **69**, 1764 (1996); doi: 10.1063/1.117478
View online: https://doi.org/10.1063/1.117478
View Table of Contents: http://aip.scitation.org/toc/apl/69/12
Published by the American Institute of Physics

Indium contamination from the indium–tin–oxide electrode in polymer light-emitting diodes

A. R. Schlatmann, D. Wilms Floet, A. Hilberer, F. Garten, P. J. M. Smulders, T. M. Klapwijk,[a] and G. Hadziioannou[b]
University of Groningen, Materials Science Centre (MSC), Laboratory of Applied Physics and Laboratory of Polymer Chemistry, Nijenborgh 4, 9747 AG Groningen, the Netherlands

(Received 17 May 1996; accepted for publication 9 July 1996)

We have found that polymer light-emitting diodes (LEDs) contain high concentrations of metal impurities prior to operation. Narrow peaks in the electroluminescence spectrum unambiguously demonstrate the presence of atomic indium and aluminum. Rutherford backscattering spectroscopy (RBS) and x-ray photoelectron spectroscopy (XPS) depth profiling data corroborate this result. An average indium concentration of 5×10^{19}atoms/cm^3 originating from the indium–tin–oxide (ITO) electrode has been found in the polymer layer. © *1996 American Institute of Physics.* [S0003-6951(96)03238-X]

Semiconducting polymers are foreseen to play an important role as active materials for electronic devices particularly in light-emitting diodes.[1,2] Among the advantages of these materials are the ease of device fabrication and the possibility to obtain large area displays by spin coating on substrates covered with transparent electrodes, which even enable flexible devices.[3] Chemical tuning of the conjugation length has resulted in colored light emission which covers the entire visible spectrum.[4–7]

To realize the prospects of these applications the stability of the device structure needed for long term operation of these light emitting diodes (LEDs) has become a crucial factor. In this respect, current research addresses the presence of impurities either as a consequence of device degradation or as the originator of the occurrence of breakdown.[8–10] Generally, it is tacitly assumed that the cleanliness of a device structure depends mainly on residuals unintentionally left from the polymer synthesis. In this letter, however, we report compelling evidence of a high level of impurities in the polymer film which originate from the electrodes prior to device operation. The devices are made according to the commonly accepted rules of cleanliness.

We use a standard cleaning procedure and work under clean room conditions. Soda lime float glass substrates are used (20 mm^2) which are covered with a standard quality, fully oxidized indium–tin–oxide (ITO) electrode of 20 nm thickness (with SiO_2 barrier coating; sheet resistance $\leqslant 200\Omega/\square$; from Merck Balzers AG). The ITO coating is made by planar dc magnetron sputtering an In_2O_3/SnO_2 (9:1) alloy target in an Ar/O_2 atmosphere, which is a commonly used method to produce thin ($<$100 nm) ITO layers with high transparency and low resistivity. A few samples were made which consist of a 30 nm (semitransparent) aluminum layer evaporated on a glass substrate. They are ultrasonically cleaned for 2 min in a series of nonpolar and polar solvents. We subsequently use xylene, 2-propanol (isopropanol), and ethanol baths followed by a rinsing step in 18 MΩ demiwater. The spin coated films are 50–150 nm thick and are optically flat and free of visible film inhomogeneities. They are dried at room temperature before slowly evaporating aluminum top electrodes of ~80 nm.

Devices were made using a sequenced conjugated block copolymer, poly[dimethylsilylene-*p*-phenylene-vinylene-(2,5,5,2″,5″- tetrabutoxy-*p*-terphenyl-4,4′-ylene)-vinylene-*p*-phenylene] hereafter conveniently abbreviated as Si-*p*PV1 (Fig. 1). In this copolymer the π-conjugation is regularly interrupted along the backbone, resulting in isolated chromophores which emit blue light. The pristine polymer is chemically pure and cannot contain any of the mentioned impurities due to the synthetic route.[11] To study the influence of the material properties on the electroluminescence spectra we also used copolymers with the same backbone but bear-

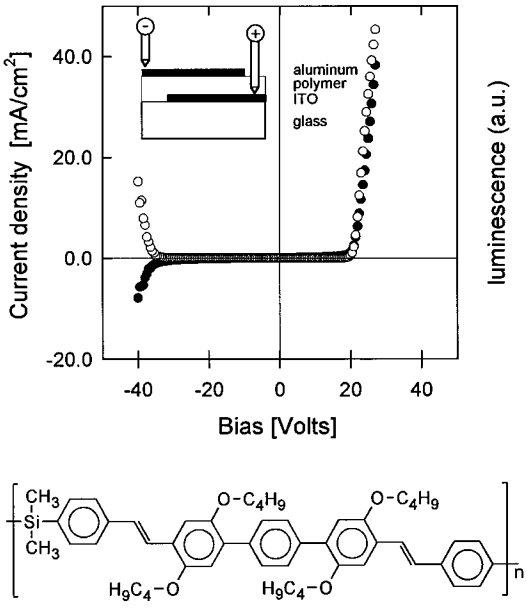

FIG. 1. Current (dots) and light (open circles) voltage characteristic of a copolymer light-emitting diode (LED). The structural formula of the copolymer Si-*p*PV1 is given. Similar copolymers with identical backbone but octyloxy or butyl instead of butoxy substituents were also used to investigate optical and morphological influences. The inset shows the cross section of the device layers and the forward bias sign.

[a]Electronic mail: t.m.klapwijk@phys.rug.nl
[b]Electronic mail: g.hadziioannou@chem.rug.nl

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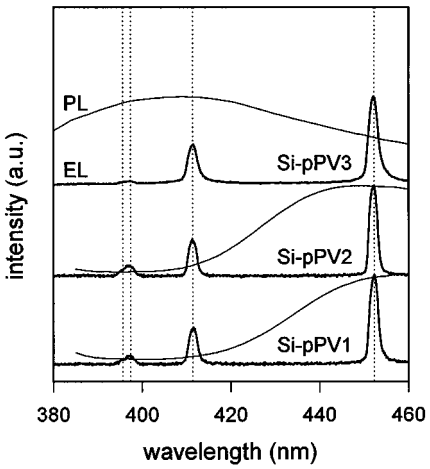

FIG. 2. Comparison of electroluminescence (EL) spectra in reverse bias with photoluminescence (PL) spectra (thin solid line) for copolymers with identical backbones but different substituents. The spectra depend on the optical properties of the copolymer for the PL but not for the EL spectra.

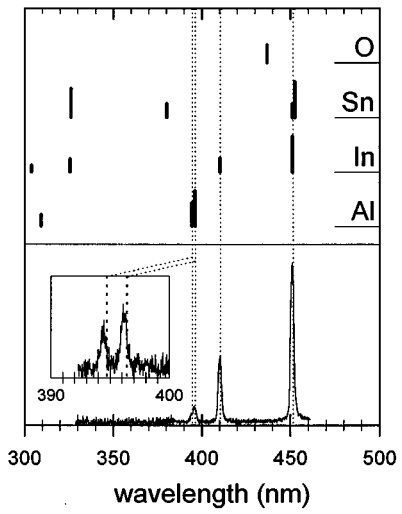

FIG. 3. Electroluminescence spectrum at reverse bias of an ITO/Si-*p*PV1/Al device structure. The peaks are compared with tabulated atomic emission lines of ^{16}O, ^{119}Sn, ^{115}In, and ^{27}Al which demonstrates that they originate from atomic impurities. The length of a line indicates its relative intensity within the spectrum of an element (determined in arc discharges) (Ref. 14).

ing other substituents [butoxy replaced by octyloxy (Si-*p*PV2) or butyl (Si-*p*PV3)].

Devices made of the copolymer Si-*p*PV1 show a current and light voltage characteristic as shown in Fig. 1. Assuming homogeneous electric field distribution these devices have a turn on in forward bias of $\sim 3\times 10^{8}$ V/m. The light output is homogeneous across the total device area and has a broad spectral distribution. Although in reverse bias the current reaches values similar to those in forward bias, transient light emission occurs at local spots (sparks) and is accompanied by severe electrode degradation. The electroluminescence (EL) spectrum only consists of four peaks having a width (FWHM) of 0.4 nm (Fig. 3). The peak positions are not influenced by the anticipated morphological change due to the variation of alkoxy substituents (Fig. 2). Changing butoxy into butyl substituents causes a blue shift of the photoluminescence (PL) but does not influence the peak positions. This demonstrates that the EL spectrum in reverse bias is not related to the properties of the polymer material (Fig. 2). To our knowledge only once before an EL spectrum was reported with a similar peak which was not identified.[12]

The wavelengths of the strongest peaks of 451.5 and 410.4 nm are in agreement with the values of the two most sensitive atomic emission lines of neutral indium which are tabulated as 451.13 and 410.18 nm, respectively[13–15] (Fig. 3). Replacing ITO for aluminum in an Al/Si-*p*PV1/Au device results in disappearance of these two peaks. No emission lines have been observed from tin or oxygen (Fig. 3). Tin has strong emission lines at 452.47, 451.13, and 380.10 nm, but no line around 410 nm.[13–15] A dedicated search did not reveal an emission line at 380 nm. We conclude, therefore, that only indium atoms originating from the ITO electrode cause these two observed emission lines. In the same way the peaks at 396.4 and 394.7 nm (inset Fig. 3) are readily attributed to the two most sensitive emission lines of neutral aluminum which are tabulated as 396.15 and 394.40 nm, respectively.[13–15] The identification of this EL spectrum demonstrates unambiguously the presence of atomic impurities in the polymer film.

To further substantiate the presence of indium impurities in the polymer film, we have determined the relative abundance of the elements in the polymer films as a function of thickness by means of XPS combined with Ar-ion sputtering. A depth profile has been taken from the aluminum top electrode towards the ITO (Fig. 4). The change of the most abundant element from Al to C determines the location of the aluminum-polymer interface region. From this point on, the characteristic signal of the In 3*d* doublet at binding energies of 443.9 and 451.4 eV has been measured. This In signal does not result from ITO which is exposed to the surface by pinholes because we did not observe any Sn signal. On a glass/ITO reference sample a Sn signal is observed with a 1:7 ratio to In. After the final sputter treatment the thickness of the polymer film remaining was determined to be 50 nm which is too thick to uncover parts of the ITO electrode by

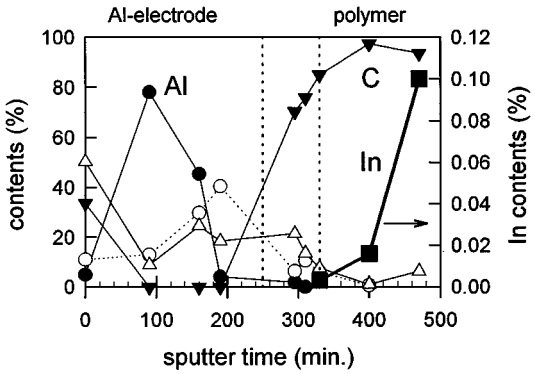

FIG. 4. Relative amounts of most important elements indentified by XPS on a ITO/Si-*p*PV1/Al device structure as function of sputter time. The vertical dotted line indicates the electrode-polymer interface region. Elements: aluminum (●), aluminum bound to oxygen (○), oxygen (△), indium (■), (carbon (▼).

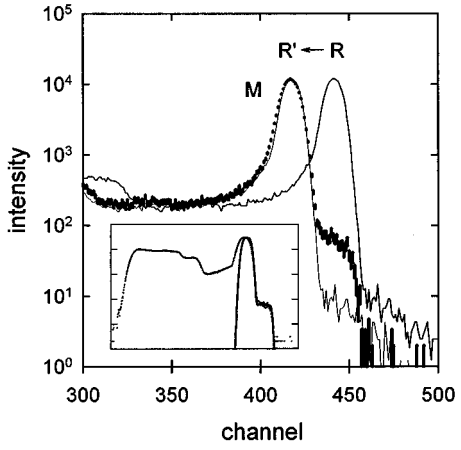

FIG. 5. Main peak in RBS of a glass/ITO reference sample (denoted *R*, solid line) and a glass/ITO/polymer sample (denoted *M*, bars) taken at 165°. The energy of scattered ions is proportional to the channel number (2.05 keV/ch). The inset shows a complete RBS spectrum taken at 105° compared with the simulated spectrum (solid line).

surface roughness. We conclude that indium is present throughout the polymer film confirming the results of the EL spectra. The ratio of the number of indium to carbon atoms reaches a value of 0.1–93.6 inside the polymer film, which equals 0.11%.

We additionally used RBS to determine the amount of impurities. A Van de Graaff acelerator produced 1 MeV He^{2+}-ions (α's) in a 4 nA beam with a spot size measuring 0.4 mm^2. Spectra of a glass/ITO/Si-*p*PV1 and a reference glass/ITO sample are plotted in Fig. 5. The main peak (*M*, bars) at high kinetic energies results from ^{115}In and ^{119}Sn in the ITO electrode. The spectrum corresponds to a shifted reference spectrum (R', thin solid line). This comparison reveals a significant yield (''plateau'') at the position of the $^{115}In/^{119}Sn$ peak of the reference spectrum which confirms the presence of ^{115}In in the polymer layer. We exclude the possibility that the plateau is due to pinholes in the film by careful optical inspection of the spots where the RBS spectra have been recorded.

We can extract an average density of indium atoms in the polymer layer by simulation of this experiment using the well-known Rutherford cross section and tabulated stopping powers. The polymer film is represented by a carbon layer with a density of 1 g/cm^3 contaminated with an unknown homogeneous indium concentration. A simulated RBS spectrum contains contributions from indium in the ITO electrode and the polymer layer applied on top. Both peaks are normalized to the area under the measured spectrum, from which a ratio is determined of the indium concentration in the polymer layer to the ITO electrode (inset Fig. 5). We have found a concentration ratio of 1:543 which implies an average ^{115}In concentration of 5×10^{19} atoms/cm^3. This is equivalent to an atomic indium to carbon ratio of 1:1000 (or 0.10%) when we take the mass of indium and tin to be equal, a measured stoichiometric ratio for In:Sn:O of 7:1:21, and an average density for ITO of 7.1 g/cm^3. This value agrees very well with the value of 0.11% found by XPS measurements.

The two electrodes in a sandwich structure differ from a fabrication point of view. One electrode—usually transparent ITO— is applied on a substrate while the other electrode has to form a metallic layer during evaporation on top of the organic layer.[16–18] When used as the top electrode indium was observed by Hirose *et al.* not to form a metallic layer until long after the beginning of the evaporation process, and it was concluded that it is highly diffusive in organic materials; aluminum behaves similarly but to a lesser extent, tin formed continuous metallic layers directly.[18] Our study shows that although the ITO electrode is known to form an excellent electrode on a glass substrate, it heavily contaminates the polymer layer spin coated on top.

We thank A. Heeres for assistance in carrying out the XPS measurements. This work is part of the research program of the ''Stichting Scheikundig Onderzoek in Nederland'' (SON) and ''Stichting voor de Technische Wetenschappen'' (STW), which are financially supported by the ''Nederlandse Organisatie voor Wetenschappelijk Onderzoek'' (NWO).

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